

GROUND STATE CONFORMATIONS AND EXCITED STATE REACTIVITIES OF TETRAHYDRO-1,4-NAPHTHOQUINONES IN THE SOLID STATE

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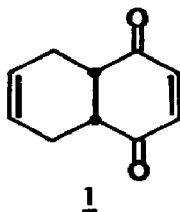
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The solid state photochemistry of substrates possessing the 4a $\beta$ ,5,8,8a $\beta$ -tetrahydro-1,4-naphthoquinone ring system, 1, has been studied at wavelengths greater than 340nm. The X-ray crystal structures of these substrates revealed a common ground state conformation irrespective of substitution. Despite their identical ground state conformations, four different reactivity patterns emerged.



Intermolecular  $[\pi^2 + \pi^2]$  cycloaddition to centrosymmetric dimers was the reaction path for substrates which have crystal structures in which adjacent pairs of molecules within a crystallographic cell are related by a centre of symmetry with the reacting double bonds oriented parallel and at a centre-to-centre separation of  $\leq 4.04\text{\AA}$ .

Intramolecular hydrogen abstraction by an oxygen of an excited carbonyl moiety proceeding via a five-membered cyclic transition state occurred in substrates which lacked the intermolecular orientation necessary for dimerization but which had the prerequisite  $\beta$ -hydrogen in the plane of the carbo-

nyl group and within a distance of  $\leq 2.58\text{\AA}$  of the oxygen. The  $H_{\beta}$ -O-C angle in all cases was very close to the optimum angle for efficient hydrogen abstraction by the n-orbital of oxygen.

Intramolecular  $\gamma$ -hydrogen abstraction by the  $\beta$ -carbon of an excited enone system became the predominant reaction only in substrates which are believed to have low-lying  $\Pi$ ,  $\Pi^*$  states. The distance between the hydrogen and the abstracting carbon was  $\leq 2.89\text{\AA}$ . Since the abstracting orbital in this instance is the 2p orbital of carbon, the optimum geometry for efficient abstraction differs from that which obtains for the  $\beta$ -process.

The fourth reaction type encountered in this investigation was intramolecular oxetane formation. It occurred only in one substrate which lacked the prerequisites for all the other three processes. There are indications that this process is the least preferred photochemical reaction pathway for these compounds.

Our results on photochemical hydrogen abstractions of both the  $\beta$ - and  $\gamma$ - types suggest that under favourable conditions such abstractions can occur over distances at least as great as the sum of the van der Waals radii of hydrogen and the abstracting atom.

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